$Fe(NO)_2$ BOUND METALLODITHIOLATES AS PENDANT BASES: AN ILLUSTRATION IN BIOMIMETICS

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

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Literature Review

Clean energies, as solar and wind power, have been used to produce electric energy, but the storage of electric power in batteries is not sufficient, and the production of batteries also generates waste. Keeping these energies in chemical bonds, the H-H bonds, would give a more sufficient way since the later use of this chemical bond energy will only generate water releasing to the atmosphere. But the efficiency of utilizing the electricity energy for hydrogen production is still ineffective. An efficient catalyst is needed to increase the efficiency and lower the cost for dihydrogen production. The [FeFe]-hydrogenase, discovered by Stephenson and Stickland in 1931 were found to be produce hydrogen in nature. [1]

The hydrogenase is an enzyme that the active sites locate on the protein molecule. The active site of [FeFe]-hydrogenase enzyme with a pendant amine base inspires a profound interest in synthesizing such heterobimetallic model complexes for dihydrogen production. [2], [3] Previous studies of $[MN_2S_2{\bullet}Fe(CO)(\eta^5\text{-}C_5H_5)]^+$ complexes indicated the hemi-lability of metallodiothiolates and their proficiency to act as a pendant base facilitating electrocatalysis for hydrogen production. [4]

Thesis Statement

This research focus on the synthesis of a similar structure, $[M(N_2S_2) \bullet Fe(Imes)(NO)_2]^+$, (M = Ni, Co(NO)) and the illustration of the free thiolate of this complex which could act like a pendant base.

Theoretical Framework

The basicity of the free thiolate of the heterobimetallic complex can be illustrated by binding with proton. Since proton is not detectable by X-ray diffraction, Au^+ complexes are used to show that the free thiolates of $[M(N_2S_2) \bullet Fe(Imes)(NO)_2]^+$ (M = Ni, Co(NO)) complexes act as a pendent base for substitute since its similar electron configuration arrangement. Thus, Au^+ complexes are surrogates of protons to mimic the protonation process for the illustration.

Project Description

Our present research pursues binding of metallodithiolates (M = Ni^{2+}, $Fe(NO)^{2+}$, $Co(NO)^{2+}$) to a carbene (Imes) stabilized $\{Fe(NO)_2\}^9$ core that result in a thiolate bridged (μ-S) monomeric or dimeric formulation. The addition of Au^+ complexes into the bimetallic complexes results in a mimic of protonation to the free thiolate. The following isolation of Au^+ bound trimetallic intermediate that will indirectly verify the concept of thiolates as pendant bases. Synthetically, addition of an acetonitrile adduct of $[AuPPh_3]^+$ to $[M(N_2S_2) \bullet Fe(Imes)(NO)_2]^+$ (M = Ni^{2+}, $Fe(NO)^{2+}$, $Co(NO)^{2+}$) at -40 ^oC, under anaerobic conditions, will be used to trap the $[M(N_2S_2) \bullet Fe(AuPPh_3)(Imes)(NO)_2]^{2+}$ trimatallic intermediate. The synthesized $[M(N_2S_2) \bullet Fe(Imes)(NO)_2]^+$ (M = Ni^{2+}, $Fe(NO)^{2+}$, $Co(NO)^{2+}$) complexes will be characterized by X-ray diffraction and in the solution state by infrared (IR), electron paramagnetic resonance (EPR), and nuclear magnetic resonance (NMR) spectroscopy.

INTRODUCTION

In 2010, solar energy has a total consumption of 3,850,000 EJ. One way to consume is to use the solar energy to generate electric power, but there is still no efficient way for the storage of electricity power is. The traditional way to storage the electric power is using battery, but the use of battery will result in large amount of chemical waste eventually. Thus, an efficient way to store the solar energy is needed, and keep the energy in chemical bonds is a good option. Storage of the energy in H-H chemical bond, in other word, using the solar energy to produce hydrogen is more efficiency and cleaner than the traditional battery. When use the produced hydrogen, it will only generate water as the byproduct, which is not harmful to either of the environment or human health. Electrolysis of water by platinum electrode is an easy way to produce hydrogen, but the efficiency is limited by the surface area of the electrode. Increasing the use of noble metal to increase the surface area is cost effective. Thus, a low-cost catalyst for improving the effciency of hydrogen production is needed.

In 1931, hydrogenase enzyme is discovered and named by Stephenson and Stickland, which was discovered to be as a catalyst for hydrogen production with high efficiency. The hydrogenase enzyme is a combination of active sites and protein matrix. The active sites are the place where proton are reduced to generate hydrogen, and the protein matrix helps to relay proton to the active sites to improve its efficiency. Vast number of bimetallic active sites found in natural as [Fe-Fe], [Ni-Fe] and iron only hydrogenase, which inspired the research on heterobimetallic system as a catalyst for hydrogen production.

Metallodithiolates (MN_2S_2) ligands have been used for the synthesisi of heterobimetallics as redox-active ligands. Recent studies of $[MN_2S_2{\bullet}Fe(CO)(\eta_5\text{-}C_5H_5)]^+$, ($M = Ni^{2+}$, $Fe(NO)^{2+}$)

showed that the dithiolates have the ability to act as proton binding sites and enhance the hydrogen production efficiency. [4]

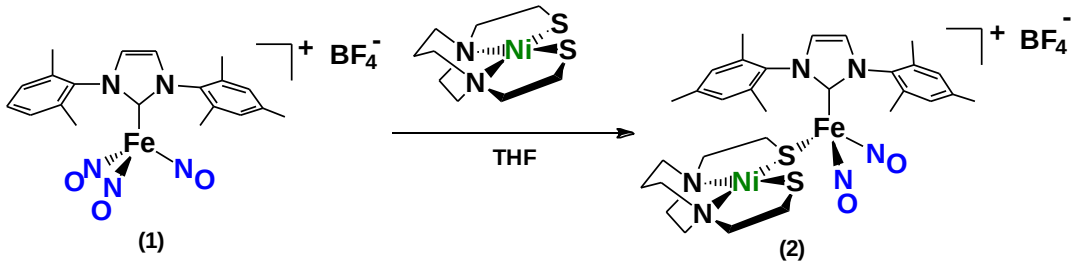
This research project is to synthesize heterobimetallic complex through reacting trinitroxyl complex (TNIC) with MN_2S_2 (M= Ni^{2+}, $Co(NO)^{2+}$) ligands, and prove that the hemi-labile dithiolate sites can act as a pendent base for proton reduction.

CHAPTER I

SYNTHESIS AND PROPERTIES OF NICKEL-IRON COMPLEX

Heterobimetallic complex, $[(Imes)Fe(NO)_2Ni(bme\text{-}dach)][BF_4]$, was synthesized by reacting 53 mg (0.1 mmol) of $Imes[Fe(NO)_3]BF_4$ with 27 mg (0.1 mmol) of Ni(bme-dach) in THF solution. The solution was dried under vacuum after ten-minute reaction and washed with ether (20 mL x 3). The product was then redissolved in THF for further reactions. The product was confirmed by IR spectroscopy with νNO at 1792 (m), 1732 (s) cm^{-1}. The reaction of $[(Imes)Fe(NO)_2Ni(bme\text{-}dach)][BF_4]$ and Ni(bme-dach) is shown in scheme 1.

Scheme 1. Synthesis of $[NiN_2S_2(Imes)Fe(NO)_2]BF_4$ complex.



Proton is usually used to illustrate if the compound can act as a base, but the structure will be difficult to observe by X-ray diffraction. Thus, Au(I) complex was used as a surrogate of proton for illustration since it has the similar valence orbital as the proton. Au(I) complex, $AuPPh_3Cl$, was used for reacting with $[NiN_2S_2(Imes)Fe(NO)_2]BF_4$ complex to prove that the hemi-labile dithiolate can act as a pendant base. The final products were crystalized and analyzed, the obtained crystal structures are shown below in Figure 1.

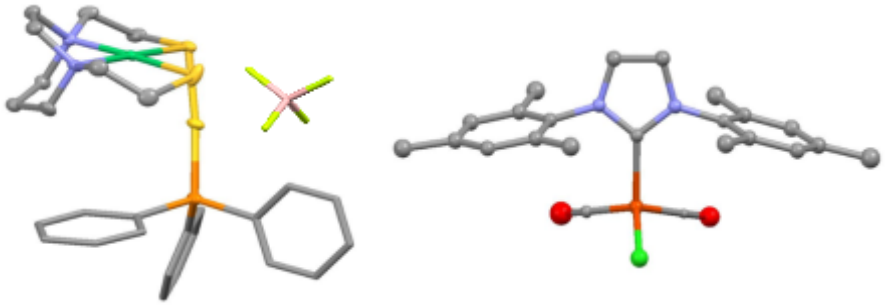


Figure 1. Crystal Structures of [{Ni(bme-dach)}$AuPPh_3$]$^+$ (as its BF_4^- salt) and (Imes)$Fe(NO)_2Cl$.

The final products showed that the proposed Fe-S bond was led to bond cleavage by the Cl^- anion, which is corresponding to the IR data of the final product that the peaks of the final product shifted to the lower wavenumber region shown in Figure 2.

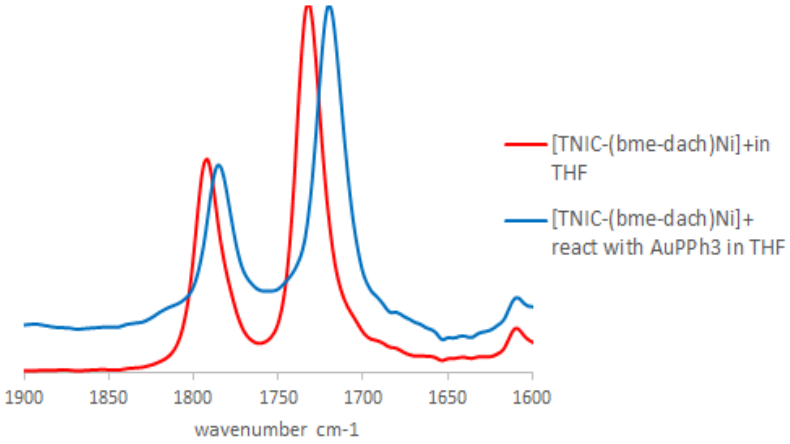


Figure 2. Solution IR of [NiN_2S_2(Imes)$Fe(NO)_2$]BF_4 (red) and the mixture of [NiN_2S_2(Imes)$Fe(NO)_2$]BF_4 and $AuPPh_3Cl$ (blue).

To eliminate the effect of Cl^- and trap the intermediate with Au-S bond, the other reaction processed with removing the Cl of $AuPPh_3Cl$ first. One equivalent of $AgBF_4$ was added to one equivalent of $AuPPh_3Cl$ in a 25 mL CH3CN solution in a round-bottom flask with aluminum film wrapped. The solution was stirred for twenty minutes and filter through “football cannula filter”

into a solution of [(Imes)Fe(NO)$_2$Ni(bme-dach)][BF$_4$] in 25-mL CH$_3$CN. The whole process was kept under -40 ^{o}C in order to trap the intermediate. The solution IR data shown in Figure 3 showed that the peaks of the final product shift to a higher wavenumber region.

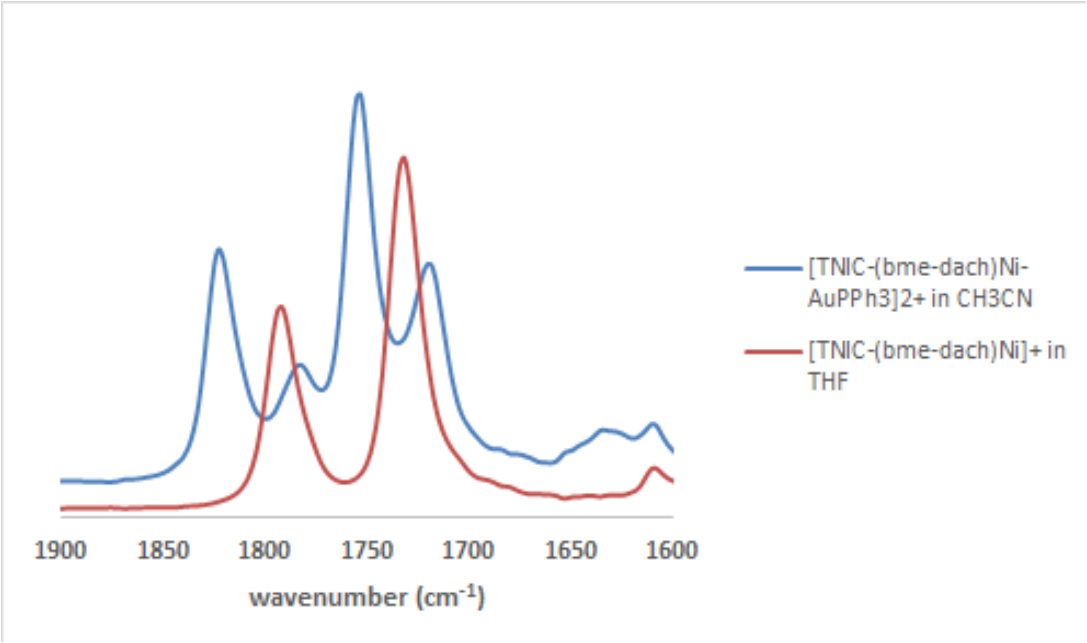
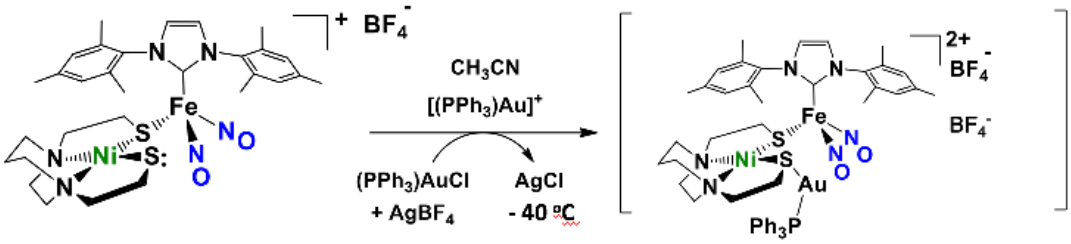


Figure 3. Solution IR of [NiN$_2$S$_2$(Imes)Fe(NO)$_2$]BF$_4$ (red) and the mixture of [NiN$_2$S$_2$(Imes)Fe(NO)$_2$]BF$_4$ and AuPPh$_3$BF$_4$ (blue).

The shift of the peaks in IR data is the evidence that the Au(I) bond to the free thiolate site, and the proposed scheme is shown below in Scheme 2. This reaction illustrated that the free thiolate in the bimetallic system acts as a pendant base.

Scheme 2. Proposed reaction of [NiN$_2$S$_2$(Imes)Fe(NO)$_2$]BF$_4$ with [AuPPh$_3$(NCCH$_3$)][BF$_4$]



CHAPTER II

SYNTHESIS AND PROPERTIES OF COBALT-IRON COMPLEX

Compared to Ni(bme-dach) ligand, Co(NO)(bme-dach) ligand is less nucleophilic, so Co(NO)(bme-dach) ligand was used to test if the free thiolate of the synthesized complex has the same ability as the one with Ni(bme-dach) ligand.

Similarly, $[(Imes)Fe(NO)_2Co(NO)(bme\text{-}dach)][BF_4]$, was synthesized by reacting 53 mg (0.1 mmol) of $Imes[Fe(NO)_3]BF_4$ with 30 mg (0.1 mmol) of Co(bme-dach) in THF solution. The solution was dried under vacuum after ten-minute reaction and washed with ether (20 mL x 3). The product was then redissolved in THF and confirmed by IR spectroscopy with νNO at 1823 (m), 1755 (s) and 1653 (w) cm^{-1}.

Au(I) complex, $[AuPPh_3][BF_4]$ was obtained in the same manner that react $AuPPh_3Cl$ with one equivalent of $AgBF_4$ under dark in 25 mL of CH_3CN for 20 minutes. The product was then filtered into a solution of one equivalent of $[(Imes)Fe(NO)_2Co(NO)(bme\text{-}dach)][BF_4]$ compelx in 25 mL of CH_3CN at -40 ºC. After ten minutes of reaction, the final product was analyzed by IR spectroscopy shown in Figure 4.

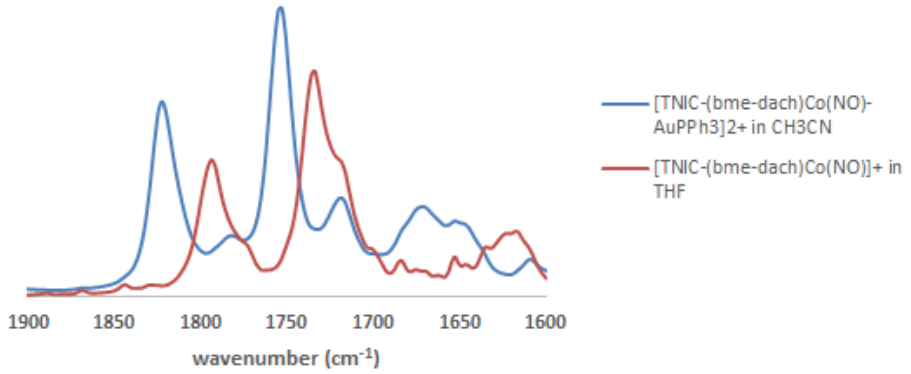
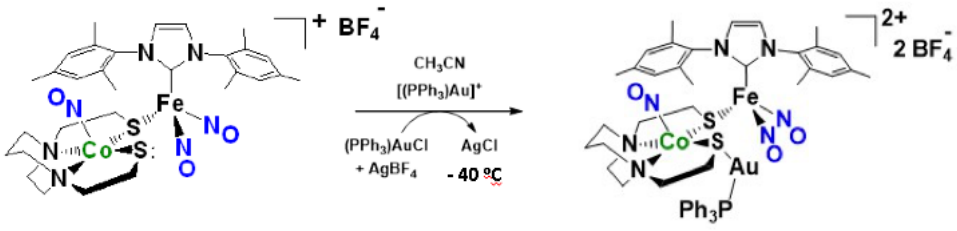


Figure 4. Solution IR of $[(NO)CoN_2S_2(Imes)Fe(NO)_2]BF_4$ (red) and and that of the reaction mixture of $[(NO)CoN_2S_2(Imes)Fe(NO)_2]BF_4$ and $[AuPPh_3][\ BF_4]$ (blue).

Compared to the peaks of the initial complex $[(Imes)Fe(NO)_2Co(NO)(bme\text{-}dach)][BF_4]$, the peaks of the final product shift to a higher wavenumber region which is a similar result as the complex with Ni(bme-dach) ligand. The evidence showed that the reaction undergoes a similar reaction route as the previous one shown in Scheme 2. The proposed reaction route is shown below in Scheme 3.

Scheme 3. Proposed reaction of $[NiN_2S_2(Imes)Fe(NO)_2]BF_4$ with $[AuPPh_3(NCCH_3)][BF_4]$



These two similar reaction routes indicate that the free thiolate of the MN_2S_2 ligand in this heterobimetallic system act as pendant bases which can be utilize in synthesis of the active sites of hydrogenase and improving the efficiency for hydrogen production by proton relaying.

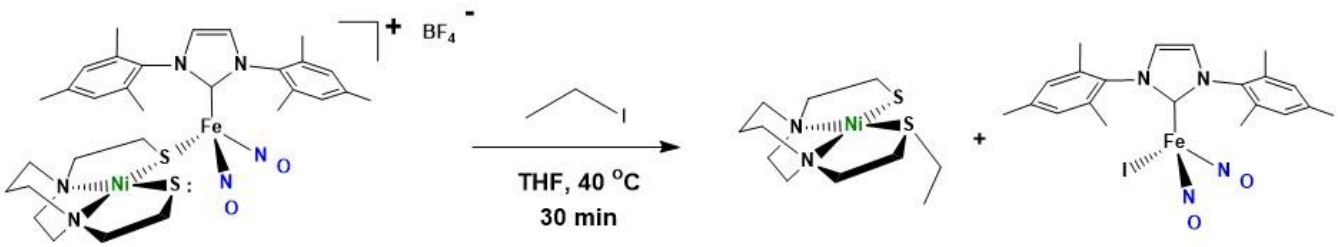
CHAPTER III

REACTIONS OF NICKEL-IRON COMPLEX WITH HALIDE COMPOUNDS

To illustrate the proposed mechanism shown in Chapter 1 that Cl- led to the bond cleavage of Fe-S bond after the formation of Au-S bond, reaction of the heterobimetallic complex Ni-Fe complex, was reacted with halide compound, ethyl iodide and benzyl bromide.

The reaction of Ni-Fe complex with ethyl iodide was done by reacting 16 mg of (0.1 mmol) ethyl iodide and 78 mg (0.1 mmol) of Ni-Fe complex in 20 mL of THF. The mixture was heated to 40 ^{o}C and stirred for 40 minutes. The solvent was dried under suction and washed with hexane (20 mL x 3) following with dissolving in 25 mL of ether. The washed solution was filtered through celite and recrystallized in ether/hexane at -28 ^{o}C. The reaction route is shown below in Scheme 4.

Scheme 4. Reaction route of Ni-Fe complex with ethyl iodide.

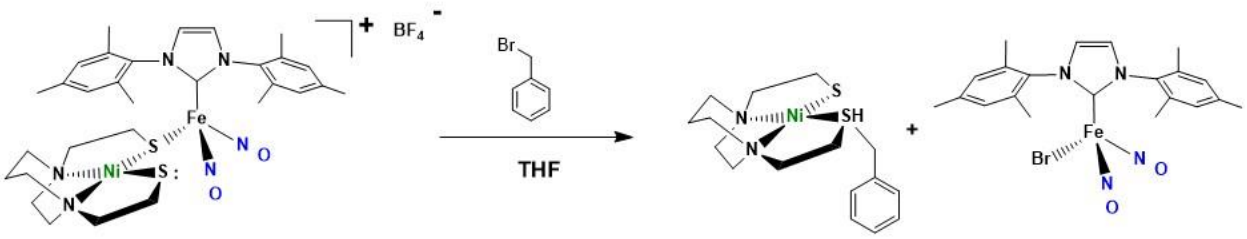


The reaction followed the same mechanism as shown in Chapter I that the iodine led to the bond cleavage of the Fe-S bond. The obtained new crystal structures are shown below in Figure 5.

Similarly, 17 mg (0.1 mmol) of benzyl bromide was reacted with 78 mg (0.1 mmol) of Ni-Fe complex in 20 mL of THF. The solvent was dried under suction and the product was washed with hexane (20 mL x 3) following with dissolving in 25 mL of ether. The washed solution was

filtered through celite and recrystallized in ether/hexane at -28 ºC. The reaction route is shown below in Scheme 5.

Scheme 5. Reaction route of Ni-Fe complex with benzyl bromide.



This reaction also followed the same mechanism as discussed above that the halide, Br- led to the bond cleavage of the Fe-S bond. The obtained new crystal structure is shown below in Figure 5.

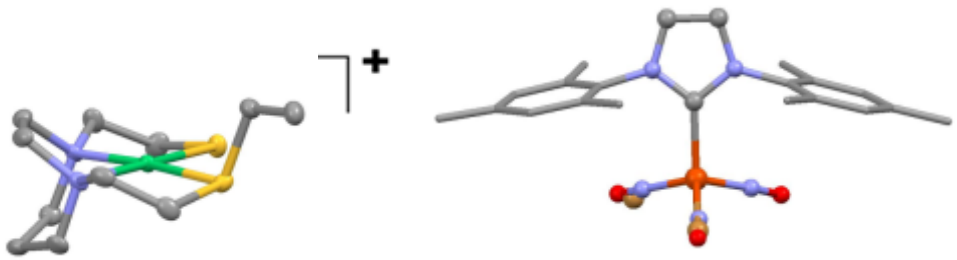


Figure 5. Two new obtained crystal structures, Ethyl-Ni(bme-dach)[BF_4] (left) and (Imes)Fe$(NO)_2$Br (right)

These two reactions also proved the proposed mechanism that the electrophile bond to the free thiolate and the halide led to the bond cleavage then. These two reactions also showed that the free thiolate can act as a pendant base for electrophiles.

CONCLUSION

The Ni-Fe heterometallic complex was synthesized successfully by reacting TNIC with NiN_2S_2 ligand, and the Co-Fe complex was synthesized in a similar manner. The free thiolate on the NiN_2S_2 (M = Ni, Co(NO)) side was proved as a pendant base by the reaction of Ni-Fe complex with $AuPPh_3Cl$. The reaction showed that bonded to the Au(I) complex to form an Au-S bond with the free thiolate on the NiN_2S_2 side and the Fe-S bond was weakened and finally led to a bond cleavage by the Cl^-. The similar reactions by reacting the Ni-Fe complex with ethyl iodide and benzyl bromide showed the similar mechanism that the free thiolate acted as a nucleophile and bonded to the electrophile. The Fe-S bond was then cleaved by the halide ions. To eliminated the effect of halide in this reaction to trap the intermediate, $AuPPh_3Cl$ was reacted with $AgBF_4$ under dark to form AgCl precipitate. The Au(I) complex was then reacted with the heterobimetallic system to form a trimetallic system is stable under -40 ^oC without the presence of Cl^-. The IR showed a shift to a higher wavenumber region which corresponds to the proposed mechanism that a trimetallic system was formed by the formation of Au-S bond. A comparison reaction by reacting the Au(I) complex with Co-Fe complex under the same condition. The IR evidence showed the same mechanism.

Thus, the free thiolates in the synthesized heterobimetallic complex, Ni-Fe and Co-Fe complexes acted as a pendant base without the presence of halide, and the trimetallic complexes were stable under low temperature. The presence of halide will lead to a bond cleavage of the Fe-S bond which dues to the formation of Au-S bond weakened the Fe-S bond.

WORKS CITED

[1] Stephenson, Marjory, and Leonard Hubert Stickland. "Hydrogenase: a bacterial enzyme activating molecular hydrogen: The properties of the enzyme." *Biochemical Journal* 25.1 (1931): 205.

[2] Lubitz, Wolfgang, et al. "Hydrogenases." *Chemical reviews* 114.8 (2014): 4081-4148.

[3] Can, Mehmet, Fraser A. Armstrong, and Stephen W. Ragsdale. "Structure, function, and mechanism of the nickel metalloenzymes, CO dehydrogenase, and acetyl-CoA synthase." *Chemical reviews* 114.8 (2014): 4149-4174.

[4] Ding, Shengda, et al. "Hemilabile Bridging Thiolates as Proton Shuttles in Bioinspired H2 Production Electrocatalysts." *Journal of the American Chemical Society* (2016).